Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) EP 0 690 344 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 03.01.1996 Bulletin 1996/01

(51) Int CL6: G03C 7/305, G03C 7/32

(21) Application number: 95304580.4

(22) Date of filing: 29.06.1995

(84) Designated Contracting States: DE FR GB NL

(30) Priority: 29.06.1994 JP 148081/94 21.09.1994 JP 226823/94

(71) Applicant: KONICA CORPORATION Tokyo 163 (JP)

(72) Inventors:

 Sugita, Shuichi Hino-shi, Tokyo (JP) Onodera, Akira Hino-shi, Tokyo (JP)

 Horiuti, Tomio Hino-shi, Tokyo (JP)

 Komatsu, Chiyoko Hino-shi, Tokyo (JP)

 Ohya, Hidenobu Hino-shi, Tokyo (JP)

(74) Representative:
Eills-Jones, Patrick George Armine
London WC1R 5LX (GB)

(54) Silver halide color photographic light-sensitive material

(57) A silver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive, a green-sensitive and a red-sensitive silver halide emulsion layer, wherein at least one of said red-sensitive silver halide emulsion layer comprises at least one compound represented by Formula 1 or Formula 2:

Formula 1

OR₁
OH
$$CONH$$
 $(R_3)_n$
OR

Formula 2

OP CONH
$$Q_2$$
 Q_3 Q_2

wherein R_1 and R_2 independently, and Q_1 and Q_2 independently represent an aliphatic group, provided that the total number of carbon atoms contained in R_1 and R_2 and in Q_1 and Q_2 is 8 or more; R_3 and Q_3 independently represent a substituent; n and m are each 0 or 1 and R and Q independently an aliphatic group, and anyl group or a heterocyclic group.

Description

Field of the Invention

This invention relates to a cyan dye-forming coupler and, more specifically, to a silver halide light-sensitive color photographic material, which contains a 1-naphthol-type cyan dye-forming coupler having in its second-position an orthoalkoxyphenylcarbamoyl group and fourth-position an aliphaticoxy group, an aryloxy group or a heterocyclicoxy group.

Background of the Invention

10

20

25

5

Heretofore, a color image is formed by imagewise exposing a silver halide light-sensitive color photographic material and undergoing color development in which a dye image is formed by the reaction of a dye-forming coupler with a paraphenylenediamine-type color developing agent.

In this photographic process, color reproduction by subtractive color system is generally employed and yellow, magenta and cyan dye images are produced.

As for cyan dye-forming coupler, phenol type and naphthol type compounds are representative and, among them, naphthol-type compounds are used in color negative films for their photographic characteristics showing sufficient light absorption in the long wavelength region and high coupling reactivity.

Heretofore, naphthol type compounds, of which second-position is substituted by a carbamoyl group have been used. However, there has been a problem that color density tends to be reduced when this type of cyan dye is processed with a fatigued bleach solution.

On the other hand, 2-arylcarbamoyl-1-naphthol-type couplers disclosed in U.S. Patent No.3,488,193, have an advantage that color density is not tend to decrease when processed with a fatigued bleaching solution, however, they have disadvantages that the maximum absorption wavelength shifts to short wavelength side in high color density area and color reproduction property is poor.

For the purpose of improving the above-mentioned disadvantages, 2-arylcarbamoyl-1-naphthol type cyan couplers disclosed in Japanese Patent Publication No.62-837475(1987), have an advantage that the maximum absorption wavelength does not shift remarkably to short wavelength side, however, the cyan couplers have a disadvantage that, in conventional color nega type developing, the maximum absorption wavelength becomes often the wavelength of not less than 700nm. A preferable wavelength range is within the range of 685nm to 700nm, so that the maximum wavelength is longer than the preferable wavelength and color reproduction is poor. Recently, although there have been a demand for a silver halide color photographic material having high sensitivity, the color forming property of the above-mentioned cyan couplers are not sufficient. Furthermore, Japanese Patent Publication No.5-40891(1993) discloses naphthol-type compounds, in which the aryl group at 2-position is substituted by a branched alkoxyl group, whereby shift of the maximum absorption wavelength was unsatisfactorily improved, however, there was still a problem that fog increases when the light-sensitive color photographic material containing this type of coupler is stored before exposure under high temperature and high humidity conditions.

Summary of the Invention

40

45

35

The first object of the present invention is to provide a silver halide color photographic light-sensitive material, which is capable of producing a dye image of enhanced sensitivity and improved image quality by employing a 1-naphthol-type cyan dye-forming coupler.

The second object of the present invention is to provide a silver halide color photographic light-sensitive material comprising a 1-naphthol-type cyan dye-forming coupler which is capable of forming a cyan dye image having a favorable spectral absorption property and, especially, having a favorable maximum absorption wavelength

The third object of the present invention is to provide a silver halide color photographic light-sensitive material which comprises a 1-naphthol-type cyan dye-forming coupler where the density loss of the cyan dye produced therefrom is reduced even when it is processed with a fatigued bleaching solution.

The fourth object of the present invention is to provide a silver halide light-sensitive color photographic material having improved storage stability before exposure.

The above-mentioned objects of the present invention have been attained by the following items.

55

Item 1: A silver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, wherein said red-sensitive silver halide emulsion layer comprises a compound represented by Formula 1 or Formula 2:

Formula 1

5

10

wherein $\rm H_1$ and $\rm H_2$ independently represent an aliphatic group, provided that the total number of carbon atoms contained in $\rm H_1$ and $\rm H_2$ is 8 or more; $\rm H_3$ represents a substituent; n is 0 or 1 and R represents an aliphatic group, an aryl group or a heterocyclic group;

15

Formula 2

20

$$\begin{array}{c|c}
OH & & \\
\hline
CONH & & \\
\hline
(Q_3)_m
\end{array}$$

25

wherein Q_1 and Q_2 independently represent an aliphatic group, provided that the total number of carbon atoms contained in Q_1 and Q_2 is 8 or more; Q_3 represents a substituent; m represents 0 or 1; Q represents an aliphatic group, an aryl group or a heterocyclic group.

30

Item 2: The silver halide color photographic light-sensitive material of item 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula 6:

Formula 6

35

$$\begin{array}{c} \text{OH} \\ \\ \text{NHCONHR}_{11} \\ \\ \\ \text{N}_{11} \end{array}$$

40

wherein R_{11} represents an aryl group or a heterocyclic group; R_{12} represents an alkyl group or an aryl group, provided that R_{12} may form a group capable of forming a dimer or an oligomer with R_{11} or R_{12} ; X_{11} represents a hydrogen atom or a group capable of splitting off upon reaction with an oxidation product of a color developing agent.

45

Item 3: The silver halide color photographic light-sensitive material of item 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula A-1:

50

Formula A-1

55

$$R_{21}CON \left\{ \begin{array}{c} R_{22} \\ R_{23} \end{array} \right.$$

55

wherein R_{21} , R_{22} and R_{23} independently represent a hydrogen atom, an alkyl group, a cycloalkyl group or an aryl group.

Item 4: The silver halide color photographic light-sensitive material of item 1, wherein said -O-Q of said Formula 2 represents an aliphaticoxy group, a heterocyclicoxy group or a

$$-O \longrightarrow (NHCO)_n - R_E$$

$$(R_A)_m$$

wherein RA represents an alkyl group, a nitro group, an amino group, an alkoxyl group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, m is an integer of 0 to 1; RB represents a hydrogen atom, an alkyl group, an alkoxyl group, an alkoxycarbonyl group, an alkylamino group, an arylamino group, a nitro group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an aryloxycarbonyl group, n is an integer of 0 to 1.

Item 5: The silver halide color photographic light-sensitive material of item 1, wherein the compound represented by said Formula 1 is represented by Formula 3:

Formula 3

OCH₂CH
$$<$$
 R_4
 R_5

OCH₂CH $<$
 R_6

OCH₂CH $<$
 R_7

30

5

10

15

20

25

wherein R_4 , R_5 , R_6 and R_7 independently represent a straight-chained or branched alkyl group, provided that the total number of carbon atoms contained in R_4 through R_7 is 6 through 28; R' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

35

Item 6: The silver halide color photographic light-sensitive material of item 1, wherein the compound represented by Formula 2 is represented by Formula 4:

Formula 4

40

45

50

wherein Q_4 represents a straight-chain, branched or cyclic alkyl group; Q_5 represents a tertiary alkyl group having 4 to 20 carbon atoms or a five member or six-member cyclic alkyl group; Q' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

Item 7: The silver halide color photographic light-sensitive material of item 6, wherein said -O-Q' of said Formula 4 represents an aliphaticoxy group, a heterocyclicoxy group or a

$$-0 - \left(\begin{array}{c} (NHCO)_{n} - R_{B} \\ (R_{A})_{m} \end{array} \right)$$

wherein R_A represents an alkyl group, a nitro group, an amino group, an alkoxyl group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, m is an integer of 0 to 1; R_B represents an alkyl group, an alkoxyl group, an alkoxycarbonyl group, an alkylamino group, an arylamino group, a nitro group, a hydroxyalkyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an aryloxycarbonyl group, n is an integer of 0 to 1.

Item 8: The silver halide color photographic light-sensitive material of item 2, wherein the compound represented by Formula 1 or Formula 2 and the compound represented by Formula 6 are contained in a molar ratio of 1:1 to 1:10.

Item 9. The silver halide color photographic light-sensitive material of item 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of 1×10^{-3} mol to 8×10^{-1} mol per mol of silver halide.

Item 10: The silver halide color photographic light-sensitive material of item 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of 1×10^{-2} mol to 8×10^{-1} mol per mol of silver halide.

Herein below, the cyan dye-forming coupler represented by Formula 1 will be described in detail.

As for the aliphatic group represented by R_1 and R_2 , straight-chained, branched or cyclic alkyl group, an alkenyl group and an alkynyl group, which may have a substituent, can be mentioned.

The aliphatic group represented by R includes preferably, those having 4 to 20 carbon atom such as, for example, butyl group, iso-butyl group, pentyl group, neo-pentyl group, isopentyl group, hexyl group, cyclohexyl group, octyl group, 2-ethylhexyl group, decyl group, dodecyl group, 2-methyloctyl group, 2-butyloctyl group, 2-hexyldecyl group, 5,7-dimethyloctyl group, 3,5,5-trimethylhexyl group and hexadecyl group.

The aliphatic group represented by R_2 includes preferably an alkyl group having 1-20 carbon atoms such as, for example, methyl group, ethyl group, propyl group, iso-propyl group and those mentioned concerning R_1 . The total number of carbon atoms contained in R_1 and R_2 is 8 or more, and it is preferably to 10 to 32 and, more preferably, at least one of them is a branched alkyl group.

R₃ represents a substituent including, for example, an aliphatic group, an aryl group, a halogen atom, a hydroxyl group, an amino group, a carbonamide group, a sulfonamide group, a ureide group, an acyloxy group, an aliphatic thio group, an aryl thio group and a sulfamoylamine group.

As for the aliphatic group represented by R in Formula 1, a straight-chained, branched or cyclic alkyl group having 1 to 30 carbon atoms and a substituted alkyl group are preferable and, a substituted alkyl group having 2 to 30 carbon atoms is more preferable. As for the substituent for the substituted alkyl group, for example, a carboxyl group, an aliphaticoxy carbonyl group, an aliphatic oxy group, an aryl oxy group, an aliphatic thio group, an aryl thio group, a sulfonyl group, an acyl group, a carbamoyl group, a sulfamoyl group, an acylamino group, a sulfonamido group, a halogen atom, a ureido group, a urethane group, an acyloxy group, an oxalyl group and an oxamide group can be mentioned.

As for the aryl group for R, substituted or unsubstituted phenyl or naphthyl group is preferable. And, a substituted phenyl group having 6 to 30 carbon atoms is especially preferable. As for the substituent of the substituted phenyl group, for example, those groups mentioned as the substituent for the substituted alkyl group for R can be mentioned.

As for the heterocyclic group for R, a five-member or six-member heterocyclic ring containing therein at least one hetero atom selected from nitrogen, oxygen and sulfur, or a fused ring formed from the above-mentioned five-member or six-member heterocyclic ring and another aromatic ring or a heterocyclic ring is preferable, and these fused rings may be substituted by a proper substituent, such as those mentioned as the substituent for the substituted alkyl group represented by R.

As R, an aliphatic group or an aryl group is preferable. Among compounds represented by Formula(I), especially preferable compound can be presented by Formula 3.

55

5

10

15

20

25

35

Formula 3

$$OCH_2CH < \frac{R_4}{R_5}$$
 $OCH_2CH < \frac{R_4}{R_5}$
 $OCH_2CH < \frac{R_4}{R_5}$

wherein R_4 , R_5 , R_6 and R_7 independently represent a straight-chained or branched alkyl group, provided that the total number of carbon atoms contained in R₄ through R₆ is 6 through 28; R' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

As for the example of the substituent for the substituted alkyl group or the substituted phenyl group represented by R', those groups mentioned as the examples of the substituent for the substituted alkyl group in the aliphatic group as R can be mentioned.

Next, the cyan dye-forming coupler represented by Formula 2 is described in detail:

The aliphatic group represented by $\mathbf{Q_1}$ and $\mathbf{Q_2}$, is straight-chained, branched or cyclic alkyl, alkenyl or alkynyl group, and the aliphatic group may have a substituent. As for the aliphatic group represented by Q1, an alkyl group having 4 to 20 carbon atoms, is preferable, and the alkyl group preferable includes, for example, butyl group, iso-butyl group, pentyl group, neo-pentyl group, iso-pentyl group, hexyl group cyclohexyl group, octyl group, 2-ethylhexyl group, decyl group, dodecyl group, 2-methyloctyl group, 2-butyloctyl group, 2-hexyldecyl group, 5,7-di-methyloctyl group, 3,5,5-trimethylhexyl group and hexadecyl group. As for the aliphatic group represented by Q2, an alkyl group having 2 to 20 carbon atoms is preferable and, more preferably, a branched or a cyclic alkyl group having 4 to 20 carbon atoms, including, for example, sec-butyl group, tert-butyl group, 1,1,3,3-tetramethylbutyl group, cyclopentyl group, cyclopexyl group, 1-ethyl-1-methylpropyl group, 1-ethyl-1-methylpentyl group, 1-hexyl-1-methylnonyl group, bicyclooctyl group, admantyl group. The total number of carbon atoms contained in Q_1 and Q_2 is 8 or more, and it is preferably to 10 to 32.

Q3 represents a substituent, and a substituent preferable includes, for example, an aliphatic group, an aryl group, a halogen atom, a hydroxyl group, an amino group, a carbonamide group, a sulfonamido group, a ureido group, an acyloxy group, an aliphatic oxy group, an aliphatic thio group, an aryl thio group and a sulfamoylamino group.

As for the aliphatic group represented by Q in Formula 2, a straight-chained, branched or cyclicalkyl group having 1 to 30 carbon atoms and a substituted alkyl group are preferable and, especially, a substituted alkyl group having 2 to 30 carbon atoms is preferable. As for the substituent for the substituted alkyl group, for example, a carboxyl group, an aliphaticoxycarbonyl group, an aliphaticoxy group, an aryloxy group, an aliphaticthio group, an arylthio group, a sulfonyl group, an acyl group, a carbamoyl group, a sulfamoyl group, an acylamino group, a sulfonamido group, a halogen atom, a ureido group, a urethane group, an acyloxy group, a cabamoyloxy group, a hydroxyl group, an aryl group, a heterocyclic group, a cyano group, a nitro group, an amino group, an oxalyl group and an oxamide group can be mentioned.

As for the aryl group for Q, substituted or unsubstituted phenyl or naphthyl group is preferable. And, a substituted phenyl group having 6 to 30 carbon atoms is especially preferable. As for the substituent of the substituted phenyl group, for example, those groups mentioned as the substituent for the substituted alkyl group for Q can be mentioned,

As for the heterocyclic group for Q, a five-member or six-member heterocyclic ring having therein at least one hetero atom selected from nitrogen, oxygen and sulfur, or a fused ring formed from the five-member or six-member heterocyclic ring and another aromatic ring or a heterocyclic ring is preferable, and these fused rings may be substituted by a substituent, such as those mentioned as the substituent for the substituted alkyl group represented by Q.

As Q, an aliphatic group or an aryl group is more preferable.

Among compounds represented by Formula 2, especially preferable example, one represented by Formula 4 can be mentioned:

50

5

10

15

20

25

35

40

45

Formula 4;

wherein Q4 represents a straight-chain, branched or cyclicalkyl group such as those mentioned above as the examples of Q1; Q5 represents a tertiary alkyl group having 4 to 20 carbon atoms such as tert-butyl group, tert-amyl group, 1,1,3,3-tetramethylbutyl group, 1-ethyl-1-methylpentyl group, 1-hexyl-1-methylnonyl group, bicyclooctyl group and adamantyl group or a five member or six-member cyclicalkyl group such as cyclohexyl group; Q' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

As for the examples of the substituent for the substituted alkyl group or the substituted phenyl group represented by Q', those groups mentioned above as the substituent for the substituted alkyl group in the aliphatic group represented by Q in Formula 2 can be mentioned.

Hereunder, compounds represented by the above-mentioned Formulae 6 and A-1 will be described in detail.

As for the aryl group represented by R_{11} or R_{12} , for example, a phenyl group and a naphthyl group can be mentioned. As for the substituent for the groups represented by R_{11} or R_{12} , for example, a halogen atom, a nitro group, a cyano

group, an alkyl group, an aryl group, an amino group, a hydroxy group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkoxysulfonyl group, an aryloxysulfonyl group, a carbamoyl group, a sulfamoyl group, an acyloxy group, a carbonamido group and sulfonamido group can be mentioned.

Preferable number of the substituent is preferable to be 1 to 5, provided that when there are two or more of substituents, they may be either same or different.

Preferable substituent on R₁₁ are a halogen atom, an alkylsulfonyl group and a cyano group.

Preferable group as R₁₂ is one represented by Formula B;

Formula B

$$(R_{14})_{K}$$
 $J-R_{13}$

35

50

30

5

10

20

wherein, J represents an oxygen atom or a sulfur atom; k represents an integer of 0 to 4; 1 represents zero or one, provided that when k is two or more, the plural number of R₁₄, may be either same or different; R₁₃ represents an alkylene group, R₁₄ represents a substituent. As for the substituent represented by R₁₄, for example, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a hydroxy group, an acyloxy group, an alkylcarbonyloxy group, an arylcarbonyloxy group, a carboxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an acyl group, an acylamino group, a sulfonamido group, a carbamoyl group and a sulfamoyl group.

As for the elimination group represented X_{11} , for example, a halogen atom, an aryloxy group, a carbamoyloxy group, a carbamoylmethoxy group, an acyloxy group, a sulfonamido group and a succinicimido group can be mentioned.

As for the more specific examples, those disclosed in U.S. Patent Nos.3,476,563 and 3,749,735; Japanese Patent Publication O.P.I. Publication No.47-37425(1972), Japanese Patent Publication No. 48-36894(1973); Japanese Patent O.P.I. Publication Nos.50-10135(1975), 50-117422(1975), 50-130441(1975), 51-108841(1976), 50-120334(1975), 52-18315(1977) and 53-105226(1978), can be mentioned.

R₂₁, R₂₂ and R₂₃ independently represent a hydrogen atom, an alkyl group, a cycloalkyl group or an aryl group and, among these groups, the alkyl group is preferable.

Those groups mentioned above may have a substituent and such substituent includes, for example, an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, an acylamino group, a sulfonamido group, an alkylthio group, an arylthio group, a halogen atom, a heterocyclic group, a sulfonyl group, a sulfinyl group, a phosphonyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a cyano group, an alkoxy group, an aryloxy group, a heterocyclicoxy group, a siloxy group, an acyloxy group, a carbamoylalkoxy group, an amino group, an alkylamino group an imido group, a ureido group, a sulfamoylamino group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group and a carboxy group can be mentioned.

Herein below, specific examples represented by Formulae 1 and 2 are shown:

g	2 3	$\begin{array}{c c} conH^{-1} & 4 \\ \hline \end{array}$	$6 \mid 5 \stackrel{\sim}{\sim} (R_3)_n$	-
(1)	H _−			- C
General Formula (1)				
General				

- NHCOCH2CH2COOH	-CH2CONHCH2CH2OCH3	$- \text{NHCOCH} < C_4 H_9 \\ C_2 H_5$	-CH ₂ COOCH ₃	-сн2соон	$- \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
ı	l	i	ı	ı	I
0	0	0	0	0	0
5-CH ₂ CH C ₄ H ₉	5-CH ₂ CH C ₄ H ₉	5-CH ₂ CH C ₂ H ₅	5 – CH ₂ CH \sim C ₂ H ₅	5-CH ₂ CH C ₂ H ₅	5-CH ₂ CH C ₂ H ₅
$-\text{CH}_2\text{CH} \Big\backslash \frac{\text{C}_4\text{H}_9}{\text{C}_2\text{H}_5}$	$-\text{CH}_2\text{CH} \Big\backslash \frac{\text{C}_4\text{H}_9}{\text{C}_2\text{H}_5}$	$-\text{CH}_2\text{CH}$ $C_2\text{H}_5$	$\begin{array}{c} \text{C}_{4\text{H}_9} \\ \text{-C}_{2\text{H}_5} \\ \text{C}_{2\text{H}_5} \end{array}$	-CH ₂ CH C ₄ H ₉	$\begin{array}{ccc} \mathrm{C_4H_9} \\ -\mathrm{CH_2CH} \\ \end{array} \begin{array}{ccc} \mathrm{C_2H_5} \end{array}$
I-1	Z-I	I-3	7 -I	1-5	9-I
	$-CH_{2}CH < C_{2}H_{5} $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	-CH ₂ CH C ₂ H ₅ 5-CH ₂ CH C ₄ H ₉ 0 - CH ₂ CH C ₂ H ₅ -CH ₂ CH C ₄ H ₉ 5-CH ₂ CH C ₄ H ₉ 0 - CH ₂ CC -CH ₂ CH C ₄ H ₉ 5-CH ₂ CH C ₄ H ₉ 0 - CH ₂ CC -CH ₂ CH C ₄ H ₉ 5-CH ₂ CH C ₄ H ₉ 0 - CH ₂ CC -CH ₂ CH C ₄ H ₉ 5-CH ₂ CH C ₄ H ₉ 0 - CH ₂ CC	-CH2CH C4H9 5-CH2CH 0 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

5 10 15	æ	-CH2CH2SCH2COOH	-снсоон С ₁₂ H25	NHSO ₂ CH ₃	NO ₂	NH2	-CH ₂ CH ₂ SCHCOOH	-снсоон С ₁₂ H ₂₅	-CH ₂ CH ₂ O———NHCO-СHCH ₂ COOH	SO ₂ CH ₃	-CH2CONHCH2COOH
	R3	ı	ı	ı	1	ı	1	J	ı	1	ı
25	ri Li	0	0	0	0	0	0	0	0	0	0
30 35	R2	5-CH ₂ CH C ₂ H ₅	5 – CH ₂ CH $^{\prime}$ C ₂ H ₅	5-CH ₂ CH C ₂ H ₅	5-CH ₂ CH ₂ CH ₃	5-CH ₂ CH C ₂ H ₅	5-CH ₂ CH C ₆ H ₁₃	$5-CH_2CH$ C_6H_{13} C_6H_{23}	$5 - \mathrm{CH_2CH} \Big\backslash \frac{\mathrm{C_8H_17}}{\mathrm{C_6H_{13}}}$	$5-\mathrm{CH}_2\mathrm{CH}_2$	5 – CH ₂ CH $^{\prime}$ C ₂ H ₅
40		C4H9 C2H5	C4H9 C2H5	C4H9 C2H5	C4H9 C2H5	CH ₃	GH3	CH ₃	СН ₃	CH ₃	. С ₆ Н ₁₃ . СН ₃
45	R_1	O CH2CH C	-CH2CH	-CH2CH	-CH2CH	-CH2CH	-CH2CH /	-CH2CH /	-CH2CH /	CH2CH	-CH ₂ CH (
50	Compound No.	1-1	8-I	6-I	I-10	I-11	1-12	I-13	Ţ-14	I-15	I-16

5	R						.2H5		Н3	—NHCOCH ₂ CHCOOH С ₁₈ H ₃₇	ж
15	-	NHCOCH ₃	-сн2сн2с1	-CH2COOC12H25	——— осн	-снсоос ₃ н ₇ сн ₃	- NHCOOC ₂ H ₅	-CH2CH2CN	- NHSO ₂ CH ₃	- NHCOCI	-CH2CH2SCH2COOH
20	R3	ı	l		I	ı	l	. 1	l	1	
25	п	0	0	0	0	0	0	0	0	0	0
30 35	R2	$5-CH_2CH$ C_2H_5	5-CH ₂ CH CH ₃	5-CH ₂ CH CH ₃	5-CH ₂ CH $<$ C ₆ H ₁₃	5-(n)C ₁₂ H ₂₅	5-CH ₂ CH CH ₃	5-сн ₃	4 -CH ₂ CH $<$ C ₂ H ₅	$6-CH_2CH$ C_2H_5	$6-\text{CH}_2\text{CH}_{\sim}$
40	_	C ₆ H ₁₃ C ₄ H ₉	C ₆ H ₁₃ C ₄ H ₉	C_8H_{17} C_6H_{13}	C_8H_{17} C_6H_{13}	GH3	125	C_6H_{13}	C_2H_5	C4H9	C4H ₉ C2H ₅
45	R ₁	_CH2CH _	-CH2CH	∕анзсн	сн₂сн∠	-CH2CH	- (n) C ₁₂ H ₂₅	-CH2CH	_CH2CH	-CH2CH	-CH2CH_
50	Compound No.	I-17	I-18	I-19	0Z-I	1-21	1-22	I-23	1-24	· 1-25	I-26

5					у соон						
10	Я	-CH2CONHCH2CH2OCH3	-Сн2СН2СОН	-CH ₂ CH ₂ SO ₂ CH ₃	- NHCONH	CONH ₂	н ₂ он	→ NHCOCOOC ₂ H ₅	-СН2СН2СООС4Н9	- СООН	
	•	-сн2с	-CH2C	-CH2C	9		-СН2СН2ОН		-CH2C		\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\
20	R3	l	1	1	4-NHCOCH3	4-NHSO ₂ CH ₃	4-C1		Į.	5-C4H9(t)	ı
25	д	0	0	0	1	н	7	0	0	н	0
30	R2	$C_5H_{11}(t)$ 6- CH_2CH_2O $C_5H_{11}(t)$	6-CH ₂ CH ₂ OC ₁₂ H ₂ 5	5-CH2CONH-(CH2)-2 OCH3	5-CH ₂ CH C ₂ H ₅	$5-\mathrm{CH}_2\mathrm{CH}$ $C_2\mathrm{H}_5$	5 -CH ₂ CH $\stackrel{<}{\sim}$ C ₂ H ₅	5-(n)C6H ₁₃	$5\text{-CH}_2\text{CH} \atop C_6\text{H}_{13}$	$^{4\mathrm{-CH_2CH}}_{\mathrm{C}_{2\mathrm{H}_5}}$	5-CH ₂ CH C ₂ H ₅
40		9-9	D-9	2-C	2-0	5-0	5-0	2- (2-c	4-(5-(
45	R ₁	$-\mathrm{CH}_2\mathrm{CH}\Big\backslash_{\mathbb{C}_2\mathrm{H}_5}$	$\begin{array}{c c} C_4H_9 \\ -CH_2CH \\ C_2H_5 \end{array}$	$\begin{array}{c} C_{L}H_{S} \\ -CH_{2}CH \\ C_{2}H_{5} \end{array}$	-CH ₂ CH C ₄ H ₉	-CH ₂ CH C ₂ H ₅	$-\text{CH}_2\text{CH} \subset \text{C}_2\text{H}_5$	- (n) C ₆ H ₁₃	-СН3	$-\text{CH}_2\text{CH} \subset \text{C}_2\text{H}_5$	-G2,G3,
50	Compound No.	I-27	1-28	I-29	I-30	I-31	I-32	I-33	I-34	1-35	I-36

EP 0 690 344 A1

			1		
R ₁ R ₂ n		ជ	1	R3	x
					CH ₂ SC ₁₂ H ₂₅
$-CH_2CH_2$ 5-(n)C ₄ H ₉ 0		0		1	z Z
C6H13		-			
			- 1		>
CH ₃ CH ₃ CH ₃ O		-		1	NHCOCH2CH2COOH
CH ₃ CH ₃ CH ₃		>			
- (n) C ₁₂ H ₂₅ 5-CH ₂ CH ₂ 0		0	!	ı	- NHCOCH2CH2COOH
	CH ₃				
- (n) C12H25 5-CH2CH		0		ı	-CH2COOC2H5
CH ₃			. 1		
C4H9		(NO ₂
C2H5 C2H5		>			CH ₂ OH

EP 0 690 344 A1

10		OX.	NHCOCH ₂ CH ₂ COOH	-CH2CONHCH2CH2OCH3	-сн2соосн3	-снсоон 	MHCOCH ₂ CHCOOH C ₈ H ₁₇	NHCOCH2CH2COOH
20		m						
		m Q3	- 0	- 0	- 0	0	0	- 0
25								
30	$\begin{pmatrix} 0.01 \\ 2 \\ \\ 6 \\ 5 \end{pmatrix} \begin{pmatrix} 4 \\ 4 \\ 5 \end{pmatrix} \begin{pmatrix} 0.01 \\ 0.02 \end{pmatrix}$	02	CH ₃ CH ₃ 5-C-CH ₂ -C-CH ₃ CH ₃ CH ₃	CH ₃ C CH ₃ CH ₃	G3 C- G3 G3	CH ₃ C CH ₃ CH ₃	CH_3 CH_3 $5-C-CH_2-C-CH_3$ CH_3 CH_3	CH ₃ CH ₃ 5-C-CH ₂ -C-CH ₃ CH ₃ CH ₃
35	O CONH		g-7-g	-CG	-C-CH2	GH3 -C-CH2 GH3	CH ₃ -C-CH ₂ CH ₃	G-C-G
40	8			7.	·.	5-	Ţ,	
45	Formula (2)	Q1	- (n) C ₈ H ₁₇	-(n)C8H17	-(n)CgH17	-(n)C ₈ H ₁ 7	-(n)C ₈ H ₁ 7	-CH2CH CH3
50	General F	Compound No.	II-1	11-2	II-3	II-4	· II-5	9-II

5 10 15	Ø	-NHCOCH2CH-COOH C8H17	-сн2соосн3	-сн2соон	CH2CONHCH2CH2OCH3	-CH ₂ CH ₂ O-С - NHCOCHCH ₂ COOH	-сн- (сн ₂) _{то} соон С ₆ н ₁₃	-CH ₂ CH ₂ O	-CH2COOC12H25
	0 3	l	ı	i	i	1	1	ı	1
25	E	0	0	0	0	0	0	0	0
30 35	Q2	c_{H_3} c_{H_3} $5-c_{-}$ $c_{H_2}-c_{-}$ c_{H_3} c_{H_3}	СН ₃ СН ₃ 5-С-СН ₂ -С-СН ₃ СН ₃ СН ₃	$\begin{array}{cccc} \text{CH}_3 & \text{CH}_3 \\ & & \\ & & \\ & & \\ & \text{CH}_3 & \text{CH}_3 \end{array}$	СН3 СН3 5-С-СН2-С-СН3 СН3 СН3	сн ₃ 5—с—сн ₂ сн ₃ сн ₃	сн ₃ 5— с— сн ₃ сн ₃	сн ₃ 5— ç— сн ₃ сн ₃	CH ₃ 5-C-CH ₂ CH ₃ CH ₃
40		H3 H3	H ₃	H ₃	Н3 Н3			ž	35
45	0,	-CH ₂ CH CH ₃	-CH2CH CH3	-CH2CH CH3	-CH2CH CH3	- (n) C ₈ H ₁ 7	- (n) C8H17	- (n) C ₁₂ H ₂₅	- (n) C ₁₂ H ₂₅
50	Compound No.	7	8-II	6-II	II-10	II-11	II-12	.II-13	II-14

10	٥	-CH2CH2SO2CH3	-CH2CONHC12H25	$- \left\langle \begin{array}{c} \\ \\ \\ \end{array} \right\rangle - \text{NHCOCH}_2 \text{CHCOOH}$ $C_9 \text{H}_{17}$	-CH2CH2CHC12H25 СООН	-CH ₂ CH ₂ SCHCOOH С ₁₂ H ₂₅	Y	CH ₃ COOH
20	Ω3	1	l	1	1	1	3-с-сн ₂ сн ₃ сн ₃	1
25	E	0	0	0	0.	0	Н	0
35	02	2-5	$_{\rm CH_3}^{\rm CH_3}$ $_{\rm CH_2CH_2CH_3}^{\rm CH_3}$ $_{\rm CH_3}^{\rm CH_3}$	$\begin{array}{cccc} CH_3 & CH_3 \\ 5-C-CH_2-C-CH_3 \\ CH_3 & CH_3 \end{array}$	$_{i_6H_{13}}^{cH_{17}} = \begin{array}{c} c_{H_3} \\ 5 - c_1 - c_{H_3} \\ c_{H_3} \end{array}$	сн ₃ 5—с—сн ₃ сн ₃	СН3 	CH ₃ CH ₃ 5C-CH ₂ C-CH ₃ CH ₃ CH ₃
45	6	-CH ₂ CH C ₂ H ₅	$-\mathrm{CH_2CH} \stackrel{\mathrm{C}_4\mathrm{H}_9}{\mathrm{C}_2\mathrm{H}_5}$	$-\text{CH}_2\text{CH} \Big\backslash \text{C}_4\text{H}_9$	$\begin{array}{c} C_{B}H_{17} \\ -CH_{2}CH \\ C_{c}H_{13} \end{array}$	- (n) C ₁₆ H33	-CH ₂ CH ₃	-(n)C8H17
50	Compound No.	II-15	II-16	11-17	11-18	II-19	11-20	11-21

5					— соон		2СООН		2СООН
10	Q	-CH2CH2NHSO2C8H17	- SO ₂ C ₁₂ H ₂₅	H ₃	- NHCONH	-NO ₂	-NHCOCH ₂ CH ₂ COOH	- СН2ОН	- NHCOCH2CH2COOH
15		-CH2CH2N	\Diamond	NHSO ₂ CH ₃		80		§ O	
20	03	1	1	ı	3-NHCOCH ₃	3-C1	1	1	1
25								0	0
1	Ħ	0	0	0	-	++	0		
30							н. У- СН. Н.	H3 H3	.н. .н.з
35	02	CH ₃ 4-C-CH ₃ CH ₃	5-C2H5	3-C2H5	CH ₃ 5-C-CH ₂ CH ₃ CH ₃	СН ₃ 5—С— СН2СН ₃ СН ₃	CH ₃ C 5 C CH ₂ C CH ₃ C	CH ₃ CH ₃ 	CH ₃ CH ₃ 5-C-CH ₂ -C-CH ₃ CH ₃ CH ₃
40	-								
45	21	- (n) C ₁₈ H ₃ 7	$-\text{CH}_2\text{CH} \underset{C_6\text{H}_{13}}{\swarrow}$	$\begin{array}{c} CgH_{17} \\ -CH_2CH \\ CgH_{13} \end{array}$	- (n) C ₆ H ₁₃	- (n) C6H ₁₃	$-\text{CH}_2\text{CH}\Big/\text{C}_2\text{H}_5$	CH ₂ CH ₅	- (n) C4H9
50	Compound No.	11-22	11-23	II-24	11-25	11-26	11-27	11-28	II-29

5						'2СООН	
10	б	СН2СООН	сн2соон	NHCOCH ₂ CH ₂ COOH	СН2ОН	-инсосн2сн2соон	СН2СООН
15		-CH2CH2SCH2COOH	-CH2CH2SCH2COOH	NHCOCH	Q Q		-CH2CH2SCH2COOH
20	Q 3	l	ţ	ı	l	1	1
25	E	0	. 0	0	0	0	0
30	02	ж. 2— сн _з 31.	ж, 2—сн ₃ ж,		лн ₃ 2— сн ₃ лн ₃	лн, С— Сиз Сиз	.сн. - сн. сн. сн.
35	O	CH ₃ CH ₃ 5-C-CH ₂ -C-CH ₃ CH ₃ CH ₃	CH ₃ 5-C-CH ₂ -C	CH3 5-C-CH3 CH3	CH ₃ 	CH ₃ 5	CH ₃
40						٠	
45	70	\bigcirc	_G, G,		-CH C2H5	-CH C2H5	-CH C2H5
50	Compound No.	II-30	II-31	II-32	II-33	II-34	II-35

Hereinbelow, representative examples represented by the above-mentioned Formulae 6 and A-1 are shown, however, the scope of the present invention shall not be limited by them.

$$\begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

$$\begin{array}{c} 6-2 \\ \text{(t) } C_5H_{11} \\ \text{(t)} \\ C_6H_{13} \end{array} \begin{array}{c} \text{OH} \\ \text{NHCONH} \\ \text{CO} \\$$

6-3 OH NHCONH SO₂C₄H₉
$$C_5H_{11}$$
 (t) C₅H₁₁ C_5H_{11} OCHCONH

6-4
$$C_{5}H_{11}(t) \longrightarrow C_{1}$$

$$C_{40}(t)C_{5}H_{11} \longrightarrow C_{4}H_{9}$$

$$C_{4}H_{9}$$

 $\begin{array}{c} \text{6-6} \\ \text{Cl} \\ \text{CgH}_{17}(\text{t}) \\ \text{OCHCONH} \\ \text{OCHCONH} \end{array}$

6-7 $C_{5}H_{11}(t) \longrightarrow OCHCONH \longrightarrow CF_{3}$ $C_{4}H_{9}$

25

35

45

6-8 $\begin{array}{c} \text{OH} \\ \text{Cl} \\ \text{(t) C}_5\text{H}_{11} \\ \end{array} \begin{array}{c} \text{OCHCONH} \\ \text{Cl} \\ \end{array}$

6-9 OH NHCONH SO₂C₃H₇ C_5H_{11} OCHCONH NHCONH

 $_{50}$ OH NHCONH CN $_{55}$ C12H25

 $C_{10}H_{21}$ OCHCONH NHCONH CN $C_{2}H_{5}$

6-12 OH NHCONH NHSO2 OC₁₂H₂₅ (CH₃)
$$_3$$
CCONH

$$\begin{array}{c} 6\text{-}13 \\ \text{(t) } C_5H_{11} & \text{OH} \\ \text{OCHCONH} & \text{NHCONH} \\ \text{C}_6H_{13} & \text{O} \\ \text{C}_8H_{17} \text{(t)} \\ \end{array}$$

6-14

(t)
$$C_5H_{11}$$
 (t) OH NHCONH SO₂ C_4H_9

C₂ H_5 OCHCONH OCHCONH OCH₃

6-16 $C_5H_{11}(t) \longrightarrow C1$ $C_5H_{11}(t) \longrightarrow CN$ $C_6H_{13} \longrightarrow F$

25 6-17 OH NHCONH C1

(t) C_5H_{11} OCHCONH OCH_2CONHCH_2CH_2OCH_3

35 6-18 OH NHCONH C1
40 $(t) C_5H_{11}$ OCHCONH CN C_4H_9 O $C_5H_{11}(t)$

55

5 C1 OH NHCONH SO $_2$ C $_4$ H $_9$ CN $_2$ C $_4$ H $_9$ OCHCONH OCHCONH OCH $_2$ CH $_2$ OH

15 6-20OH
NHCONH

CN

C12H25

OC4H9

40

*5*5

6-22

(t) C_5H_{11} OCHCONH

OCHCONH

OCH3

6-25

$$C_{16}H_{33}$$
 — CONH — ON CONHCH₂CH₂OH

40
$$6-26$$
 OH NHCONH OCOCH₃
 $C_{15}H_{31}CONH$ C1

 $\begin{array}{c} \text{6-27} \\ \text{(t) } C_8H_{17}\text{(t)} \\ \text{OCHCONH} \\ \text{C}_4H_9 \\ \text{O} \\ \text{SO}_2 \\ \text{OH} \end{array}$

$$6-29$$

OH

NHCONH

COOC₂H₅

C1

C1

C1

C1

C1

NHCONH

A

COOC₂H₅

6-30 OH NHCONH SO₂ CH₃

(t)
$$C_5H_{11}$$
 OCHCONH Cl

24

45

15
$$6-32$$

OCH₃

OH

NHCONH

NSO₂

C₁₂H₂₅

OCH₃

6-34 OH NHCONH SO₂CH₂

$$C_{15}H_{31} C_{2}H_{5} O(CH_{2})_{3}COOH$$

$$\begin{array}{c} \text{ 6-36} \\ \text{OH} \\ \text{OH} \\ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \end{array} \begin{array}{c} \text{OCHCONH} \\ \text{CH}_2 \\ \end{array} \begin{array}{c} \text{OCH}_2 \\ \text{NHCONH} \\ \end{array}$$

CNOCHCONH

OCHCONH $C_{12}H_{25}$ O(CH₂) $_2$ SCHCH $_3$ COOH

25

$$6-38$$

C1

OCHCONH

NHCONH

CO-N

OCH3

6-39

5
$$\begin{array}{c} CN \\ C_5H_{11}(t) \\ C_4H_9 \end{array} \begin{array}{c} CN \\ COHCONH \\ CI \end{array}$$

15 6-40

²⁵ 6-41

$$C_5H_{11}$$
 (t) C_5H_{11} OH NHCONH CN

 C_4H_9 OCH $_3$

40

30

$$\begin{array}{c} 6-42 \\ \\ 45 \\ \\ 6-42 \\ \\ (t) C_5H_{11} \\ \\ \\ C_2H_5 \\ \\ \\ OCH_3 \\ \end{array}$$

15

30

40

45

55

x:y = 50:50 (weight ratio)

20
$$CH_2$$
 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 $COOC_4H_9$ $COOC_4H_9$

x:y = 50:50 (weight ratio)

As for other specific examples of the phenol-type coupler having a ureido group, than those given above, for example, those disclosed in Japanese Patent O.P.I. Publication Nos.56-65134(1981), 57-204543(1982), 57-204544(1982), 57-204544(1982), 57-204545(1982), 58-33249(1983), 58-33253(1983), 58-98731(1983), 58-118643(1983), 58-179838(1983), 58-187928 (1983), 59-65844(1984), 59-71051(1984), 59-86048(1984), 59-105644(1984), 59-111643(1984), 59-111643(1984), 59-131939(1984), 59-165058(1984), 59-177558(1984), 59-180559(1984), 59-198455(1984), 60-35731(1985), 60-37557(1985), 60-49335(1985), 60-49336(1985), 60-50533(1985), 60-91355(1985), 60-107649(2984), 60-107650 (1985) and 61-2757(1986) can be mentioned.

A-1 A-2
$$C_{11}H_{23}CN < C_{2}H_{5} C_{11}H_{23}CN < C_{4}H_{9}$$

$$C_{2}H_{5} C_{4}H_{9}$$

Herein below, synthetic examples of the cyan dye-forming coupler represented by Formula 1 are given.

Synthesis Example 1-1(Synthesis of Compound i-1)

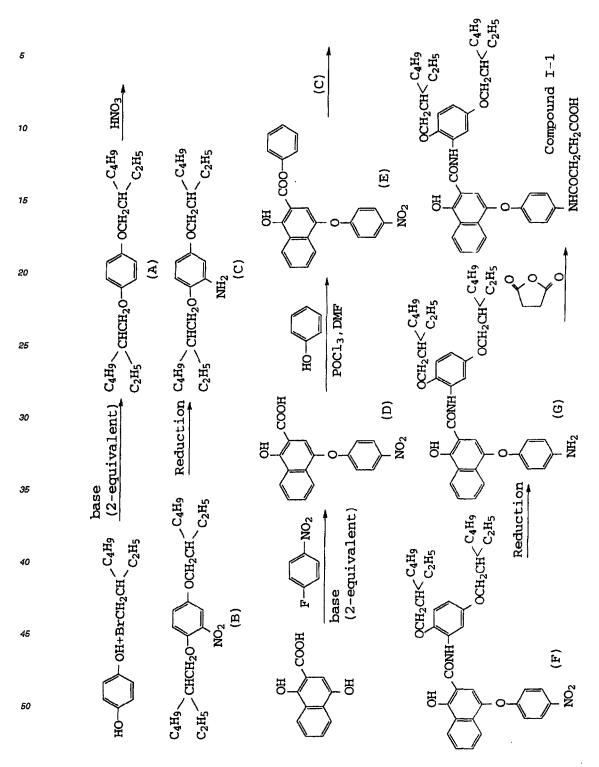
Compound I-1 can be synthesized according to the following scheme.

45

40

35

50



22 g of p-hydroquinone and 77 g of 2-ethylhexyl bromide were dissolved in 150 ml of ethanol. Next, 300 ml of ethanol solution, in which 29 g of potassium hydroxide was dissolved, was added and underwent reaction for ten hours under reflux. After filtrating off the precipitated potassium bromide the solution was condensed and extracted the reaction product by adding ethyl acetate and water, to collect an organic phase. After condensing this 40.5 g of 1,4-di-(2-ethyl-

hexyloxy)benzene(A) in the form of a colorless oil(), was obtained by vacuum distillation (a temperature range of 200 to 203 °C, a pressure condition is 3 mmHg).

80 ml of chloroform was added to 27 g of (A), and to this 10 g of 65% nitric acid was added dropwise while cooling down the solution at 0 to 3°C. While maintaining cooling, the solution was stirred for one hour and, then, water was added to wash an organic phase. After washing with 5% sodium hydrogencarbonate and water, the organic phase was condensed and dried, to obtain 30.6 g of 2,5-di-(2-ethylhexyloxy)nitrobenzene(B) in the form of a yellowish oil. This was used in the next step without refinement.

29 g of (B) was dissolved in 30 ml of methanol and 120 ml of ethyl acetate and, to this 3 g of 5% wet Pd/C catalyst was added to underwent catalytic hydrogenation for ten hours under ordinary temperature and ordinary pressure. After completion of the reaction, the catalyst was filtered out and, by condensing and drying the filtered solution, 26 g of 2,5-di-(2-ethylhexyloxy)aniline(C) in the form of a thin-brownish oil was obtained. This was used in the next step without refinement.

250 g of 1,4-dihydroxy-2-naphthoic acid was added to 1.9 1 of N,N-dimethylformamide and, to this, an aqueous alkaline solution consisting of 103 g of sodium hydroxide and 154 ml of water was added, under nitrogen gas flow. While maintaining the inner temperature at 30°C, 172 g of 1-fluoro-4-nitrobenzene was added taking 10 minutes and stirred for two hours at the inner temperature of 45°C. The mixture was, then poured into 1.5 Kg of ice and 250 ml of concentrated hydrochloric acid, and then, solidified crude crystals were filtrated. This was further recrystallized in acetonitrile, to obtain 315 g of 1-hydroxy-4-(4-nitrophenoxy)-2-naphthoic acid (D) in the form of pale yellowish crystals

250 g of (D) and 87 g of phenol were added to 1.5 liter of chloroform and, then, after 119 g of phosphorous oxychloride was added dropwise, temperature was raised up to reflux temperature and, then under reflux 250 ml of N,N-dimethylformamide was added drowise taking about two hours and the mixture was further stirred for five hours under reflux. After leaving the reaction mixture overnight, it was condensed until the volume of the reaction mixture became about 700 ml and then 21 of methanol was added to this, precipitated crystal were filtrated to obtain 235 g of 1-hydroxy-4-(4-nitrophenoxy)-2-naphthoic acid phenyl (E) in the form of pale yellowish needle crystals.

21 g of (E) and 20 g of (c) were added to 100 ml of mesitylene and the mixture was stirred for two hours at the inner temperature at 150 to 160°C. After completion of the reaction, while maintaining heating mesitylene and phenol were distilled out under reduced pressure. After cooling down the reaction mixture to 50 to 60°C, 100 ml of 2: 1 mixed solution of ethyl acetate and methanol was added and after cooling with ice, precipitated crystal were filtrated, to obtain 20 g of 1-hydroxy-4-(4-nitrophenoxy)-N-[2,5-di-(2-ethylhexyloxy)phenyl]-2-naphthamide(F) in the form of pale yellow crystals.

17 g of (F) was dissolved in 170 ml of ethylacetate ,to this 3 g of 5% wet Pd/C catalyst was added to undergo catalytic hydrogenation for seven hours under room temperature and atmospheric pressure. After completion of the reaction, the catalyst was filtrated and, by condensing and drying the filtered solution, 16 g of 1-hydroxy-4-(4-aminophenoxy)-N-[2,5-di-(2-ethylhexyloxy)phenyl]-2-naphthamide(G) was obtained in the form of brownish oil.

4 g of (G) and 0.7 g of succinic acid anhydride were added and dissolved in 40 ml of ethyl acetate, and under reflux the solution was stirred for one hour. After completion of the reaction, water was added and extracted with ethyl acetate and the collected organic phase was condensed after washing. By refining the crude product was refined by the use of silica gel chromatography(n-hexane-ethyl acetate eluate).

Thus 3.1 g of Compound I-1 was obtained in the form of white crystals.

Result of Elementary Analysis

Formula: C₄₃H₅₄N₂O₈

	C(%)	H(%)	N(%)
Calculation:	71.05	7.49	3.85
Experimental	71.02	7.53	3.83

Synthesis Example: 1-2 (Synthesis of Compound I-2)

Compound I-2 can be synthesized according to the following scheme.

55

50

20

25

35

40

OH COOH BrCH2CONHCH2CH2OCH3 OCH2CONHCH2CH2OCH3

OH OCH2CONHCH2CH2OCH3

OH OCH2CONHCH2CH2OCH3

OCH2CH
$$\begin{pmatrix} C_4H_9 \\ C_2H_5 \end{pmatrix}$$

OCH2CONHCH2CH $\begin{pmatrix} C_4H_9 \\ C_2H_5 \end{pmatrix}$

OCH2CONHCH2CH $\begin{pmatrix} C_4H_9 \\ C_2H_5 \end{pmatrix}$

53 g of 1,4-di-hydroxy-2-naphthoic acid was dissolved in one liter of N,N-dimethylformamide and thereto an aqueous alkaline solution consisting of 22 g of sodium hydroxide and 33 g of water was added dropwise under nitrogen gas flow. After stirring for 30 minutes, a solution consisting of 51 g of N-(2-methoxyethyl)-2-bromoacetamide and 200 ml of N,N-dimethylformamide were added dropwise and reacted for four hours under inner temperature condition at 42 to 44°C. Then this was poured into 400 g of ice and 85 ml of water and precipitated crystals were taken by filtration. Further, by recrystalizing with acetonitrile, 61 g of 1-hydroxy-4-(2-methoxyethylcarbamoylmethoxy)-2-naphthoic acid(H) was obtained in the form of pale greenish cotton-like crystals.

Compound I-2

3 g of (H) and 3.3 g of (C), which was synthesized in I-1 above, were dissolved in 70 ml of warmed dioxane and, thereto, a solution consisting of 2.1 g of 1,3-dicyclohexylcarbodimide and 20 ml of dioxane was added. Agitate the solution for one hour under inner temperature at 50°C and, after precipitated 1,3-dicylohexylurea by filtration was separated, the filtered solution was condensed. By refining the obtained reaction mixture by silica gel column chromatography(with n-hexaneethyl acetate type eluate), 3.8 g of Compound I-2 was obtained in the form of white crystals.

Result of Elementary Analysis

Formula: C₃₈H₅₄N₂O₇

35

20

30

40

50

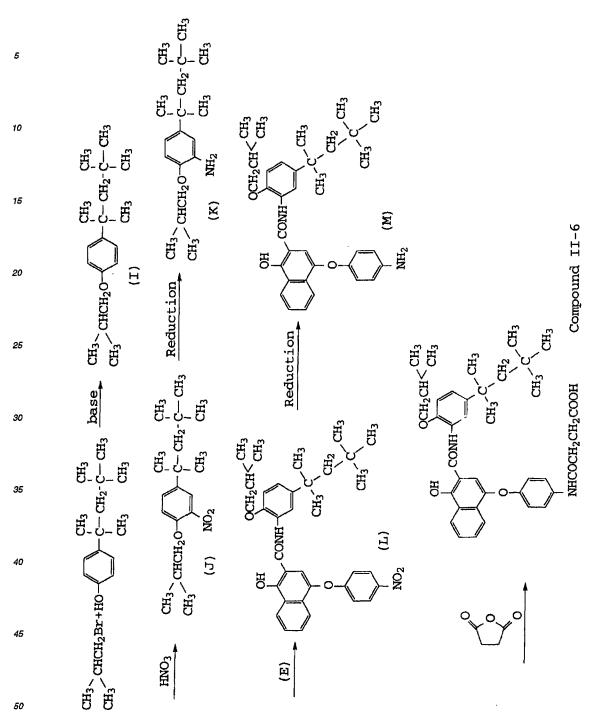
55

	C(%)	O(%)	N(%)
Calculation:	70.13	8.36	4.30
Experiment:	70.12	8.39	4.32

Synthesis examples of the cyan dye-forming coupler represented by Formula 2 of the present invention are illustrated below:

Synthesis Example: 2-1 (Synthesis of Compound II-6)

45 Compound II-6 can be synthesized according to the following scheme.



20 g of 4-(1,1,3,3-tetramethylbutyl)phenol was dissolved in 100 ml of N,N-dimethylformamide and after 15 g of isobutyl bromide to this, 18 g of potassium carbonate(K2C03) was added and stirred for eight hours under inner temperature at 80°C. After completion of the reaction, water was added to the reaction mixture, extracted with ethyl acetate and the organic phase washed with a saturated aqueous sodium chloride solution. Condensing and drying the product and then by refining it by silica gel column chromatography, to obtain 18 g of 4- isobutyloxy-(1,1,3,3-tetramethylbutyl) benzene (I) in the form of colorless oil.

8 g of (I) was dissolved in 50 ml Of chloroform and to this 5.5 ml of 61% nitric acid was added dropwise. This was

stirred for two hours under inner temperature at 40°C. After completion of the reaction, water was added to separate the organic phase and washed with water. Condensing and drying the organic phase and, then, by refining it by silica gel column chromatography with n-hexane-ethyl acetate eluate, to obtain 9 g of 2-isobutyloxy-5-(1,1,3,3-tetramethyl-butyl)nitrobenzene (J) in the form of yellowish oil.

8 g of (J) was dissolved in 50 ml of methanol and, to this, 1 g of 5% wet Pd/C catalyst was added, to undergo contact hydrogenation for three hours under room temperature and atmosheric pressure. After completion of the reaction, the catalyst was filtrated out and the filtered solution was condensed and dried to obtain 7 g of 2-isobutyloxy-5-(1,1,3,3-te-tramethylbutyl)aniline (K) in the form of brownish oil.

4 g of (E)(cf. Synthesis Example I-1) and 3 g of (K) were added into 20 ml of mesitylene and this was stirred for three hours under inner temperature at 150 to 160°C. After completion of the reaction and, while keeping heating, mesitylene and phenol were distilled off. After cooling down the reaction mixture to 50 - 60°C, 30 ml of 2:1 mixed solvent of ethyl acetate and methanol was added. After cooling down the reaction mixture with ice, precipitated crystals were filtered and 4.8 g of 1-hydroxy-4-(4-nitrophenoxy)-N-[2-isobutyloxy-5-(1,1.3,3-tetramethylbutyl)phenyl]-2-naphthamide (L) was obtained in the form of pale yellowish crystals.

4 g of (L) was dissolved in 50 ml of ethyl acetate and , to this, 0.5 g of 5% wet Pd/C catalyst was added, to undergo contact hydrogenation for eight hours under room temperature and atmospheric pressure. After completion of the reaction the catalyst was filtrated out and the filtered solution was condensed and dried to obtain 3.8 g of 1-hydroxy-4-(4-aminophenoxy)-N-[2-isobutyloxy-5-(1,1,3,3-tetramethylbutyl)phenyl]-2-naphthoamide (M) in the form of pale brownish solid.

3 g of (M) and 0.6 g of succinic acid anhydride were added to 30 ml of ethyl acetate and stirred under reflux for one and half hours. After completion of the reaction water was added and extracted with ethyl acetate. After washing with water the collected organic phase was condensed by refining the crude product, by silica gel column chromatography with n-hexane-ethyl acetate type eluate, 2.1 g Compound II-6 was obtained in the form of white crystals.

Result of Elementary Analysis: Chemical Formula: C₃₉H₄₆N₂O₇

5

10

15

20

25

30

50

55

 C(%)
 H (%)
 N(%)

 Calculation:
 71.54
 7.08
 4.28

 Experiment:
 71.51
 7.10
 4.27

Synthesis Example 2-2(Synthesis of Compound II-10)

Compound II-10 is synthesized according to the following scheme.

35

OCH₂CH
$$<$$
CH₃

CH₃

CH₃

CH₂

CH₃

CH₃

CH₃

CH₂

CH₃

Compound II-10

3 g of (H) and 2.7 g of (K)(cf. Synthesis Example 2-1 above) were dissolved in 70 ml of dioxane and, to this, 2.1 g of 1,3-dicyclohexylcarbodiimide and 20 ml of dioxane were added. The solution was stirred at inner temperature of 50 °C for one and a half hours. After filtrating off the precipitated 1,3-dicyclohexylurea, the reaction mixture solution was filtered and the filtered solution was condensed, and the crude product was obtained. The crude product was refined by silica gel column chromatography with n-hexaneethyl acetate type eluate, 3.2 g of Compound II-10 was obtained in the form of white crystals.

Result of Elementary Analysis: Chemical Formula: C₃₄H₄₆N₂O₆

	C(%)	H (%)	N(%)
Calculation:	70.56	8.01	4.84
Experiment:	70.54	8.04	4.83

In the present invention, the cyan dye-forming coupler represented by the above-mentioned Formula 1 or 2 is incorporated in at least one red-sensitive silver halide emulsion layer.

The cyan dye-forming couplers represented by the formulae 1 and 6 or formulas 2 and 6 can be used in the optional proportion, however, preferably, within a molar ratio of 1/1 to 1/10. The cyan dye-forming couplers represented by the Formulae 1, 2 and 6 may be used in the quantity of $1x10^{-3}$ to $8x10^{-1}$ mol and, more preferably, $1x10^{-2}$ to $8x10^{-1}$ mol per a mol of silver halide.

Amount of the compound represented by the Formula A-1 is preferably 0.01 to 10 g and, more preferably, 0.1 to 3.0 g per one gram of the cyan dye-forming coupler represented by Formulas 1, 2 or 6. Moreover the compound represented by the Formula A-1 may be used either one kind or two or more kinds in combination.

In order to incorporate compound represented by Formulas 1, 2, 6 or A-1 used in the present invention in a silver halide emulsion layer, it is possible to apply a method, in which the above-mentioned compound or compoundes are first dissolved in a conventionally known high boiling-point solvent, such as dibutyl phthalate, tricresyl phosphate or combination of the high boiling-point solvent and a low boiling-point solvent such as butyl acetate, either singly or in combination, respectively. Then the coupler solution is mixed with an aqueous solution containing gelatin and a surface active agent. Subsequently, after the solution is subject to emulsification, using a high-speed rotary mixer, such as a colloid mill or a ultra-sonic homogenizer, this may be incorporated into the emulsion, either directly or after it being is set, cut and washed with water.

The compound represented by Formulas 1, 2, 6 or A-1 may be incorporated in the silver halide emulsion layer either separately after separately dissolving in the high boiling-point solvent and dispersing in the above-mentioned method, or at a time. Furthermore, concerning the compounds represented by Formulas 1, 2, 6 or A-1 it is preferable that compounds are dissolved, and dispersed altogether and incorporated in the silver halide emulsion layer.

As for silver halide emulsion used in the light-sensitive material of the present invention, any kind of silver halide emulsion which is known in the art can optionally be employed.

The emulsion may undergo a conventional chemical sensitization, and can be spectrally sensitized with a conventional sensitizing dye, to make the emulsion sensitive to any pre-designed spectral region.

The silver halide emulsion can comprise one or more kinds of photographic additives such as an anti-foggant, a stabilizer, etc. As for the binder for the emulsion, it is preferable to use gelatin.

The silver halide emulsion layer and other hydrophilic colloidal layer may be hardened and can comprise a plasticizer and a dispersion containing a polymer which is insoluble or sparsely soluble in water. A coupler is used in the silver halide emulsion layer of the color photographic light-sensitive material.

It is also possible to use a colored coupler having a function as a color compensator, a competing coupler, a compound which is, upon reaction with an oxidation product of a color developing agent capable of splitting off a photographically useful fragment such as a development accelerator, a bleach accelerator, a developing agent, a solvent for the silver halide, a color toning agent, a hardener, a fogging agent, an anti-foggant, a chemical sensitizer, a spectral sensitizer, a desensitizing agent.

As for the support, for example, paper laminated with a polymer such as polyethylene, a polyethyleneterephthalate film, a baryta paper and a cellullose triacetate may be used.

In order to obtain a dye image using the light-sensitive material of the present invention, color photographic process which is generally known in the art may be applied.

The present invention can be applied to any type of silver halide light-sensitive materials known in the art, including negative-type color films, color papers and reversal-type color films.

Examples

5

10

15

30

45

50

55

Hereinbelow the present invention is further explained with reference to working examples, however, the scope of the present invention is not limited by them.

In all of the following examples, the amount of addition of the additive in the silver halide light-sensitive photographic material is given, unless defined otherwise, in terms of weight (g) a square meter of the light-sensitive material. Concerning the amount of silver halide and colloidal silver, they are expressed in terms of equivalent amount of silver.

Example 1

On a triacetylcellullose film support, respective layers, the components of which are given below, are provided in order to prepare a multi-layer silver halide light-sensitive color photographic material (Sample No.1).

First Layer: Anti-Halation Layer (HC-1)

Black colloidal silver	0.20
UV Absorbent (UV-1)	0.20
Colored coupler (CC-1)	0.05
Colored coupler (CM-1)	0.05
High boiling-point solvent (Oil-1)	0.20
Gelatin	1.5

Second Layer: Intermediate Layer (IL-1)

20

25

5

10

15

UV absorbent (UV-1)	0.01
High boiling-point solvent (C	oil-1)
Gelatin	1.5

Third Layer: Low red light-sensitive silver halide emulsion layer (RL)

	Silver iodobromide emulsion (Em-1)	0.8
30	Silver iodobromide emulsion (Em-2)	0.8
	Sensitizing dye (SD-1) 2.5x10 ⁻⁴ mols a mo	ol of silver
35	Sensitizing dye (SD-2) 2.5x10 ⁻⁴ mols a mo	ol of silver
	Sensitizing dye (SD-3) 0.5x10 ⁻⁴ mols a mo	ol of silver
	Cyan dye-forming coupler (C-A)	1.0
40	Colored cyan coupler (CC-1)	0.05
	DIR compound (D-1)	0.002
	High boiling-point organic solvent (Oil-	1)
45		0.5
	Gelatin	1.5

50

Fourth Layer: High red light-sensitive silver halide emulsion layer (RH)

5	Silver iodobromide emulsion (Em-3)	2.0		
-	Sensitizing dye (SD-1) 2.0×10^{-4} mols a	a mol of silver		
	Sensitizing dye (SD-2) 2.0x10 ⁻⁴ mols a	a mol of silver		
10	Sensitizing dye (SD-3) 0.1x10 ⁻⁴ mols a	a mol of silver		
	Cyan dye-forming coupler (C-A)	0.25		
15	Cyan dye-forming coupler (C-B)	0.05		
,,,	Colored cyan coupler (CC-1)	0.015		
	DIR compound (D-1)	0.05		
20	High boiling-point organic solvent (O	il-1)		
		0.2		
25	Gelatin	1.5		
20	Fifth Layer: Intermediate Layer (IL-2)			
30	Gelatin 0.5			

Sixth Layer: Low green light-sensitive silver halide emulsion layer (GL)

35

	Silver iodobromide emulsion (Em-1)	1.3
	Sensitizing Dye (SD-4) $5x10^{-4}$ mols a mol	of silver
40	Sensitizing dye (SD-5) 1×10^{-4} mols a mol	of silver
	Magenta dye-forming coupler (M-1)	0.25
45	Magenta dye-forming coupler (M-2)	0.25
	Colored magenta coupler (CM-1)	0.01
	DIR Compound (D-3)	0.02
50	DIR Compound (D-4)	0.020

	High boiling-point organic solvent (Oil-2)
5	0.3
	Gelatin 1.0
10	Seventh Layer: High green light-sensitive silver halide emulsion layer (GH)
	Silver iodobromide emulsion (Em-3) 1.3
15	Sensitizing Dye (SD-6) 1.5x10-4 mols a mol of silver
	Sensitizing dye (SD-7) 2.5×10^{-4} mols a mol of silver
20	Sensitizing dye (SD-8) 0.5×10^{-4} mols a mol of silver
20	Magenta dye-forming coupler (M-1) 0.05
	Magenta dye-forming coupler (M-2) 0.10
25	Colored magenta coupler (CM-2) 0.05
	DIR Compound (D-3) 0.01
30	High boiling-point organic solvent (0i1-2)
-	0.2
	Gelatin 1.0
35	Eighth Layer: Yellow Filter Layer (YC)
40	Yellow colloidal silver 0.1
	Anti-dye staining agent (SC-1) High boiling-point organic solvent (Oil-3) Gelatin 0.1 0.8
45	Ninth Layer: Low blue light-sensitive silver halide emulsion layer (BL)
	Silver iodobromide emulsion (Em-1) 0.25
50	Silver iodobromide emulsion (Em-2) 0.25

Sensitizing dye (SD-10)

	$7x10^{-4}$ mols a mo	l of silver
5	Yellow dye-forming coupler (Y-1)	0.5
	Yellow dye-forming coupler (Y-2)	0.1
10	DIR Compound (D-2)	0.01
	High boiling-point organic solvent (Oil	-2)
		0.3
15	Gelatin	1.0
	Tenth Layer: High blue light-sensitive silver halide emulsion layer (BH)	
20	Silver iodobromide emulsion (Em-4)	0.4
	Silver iodobromide emulsion (Em-1)	0.4
25	Sensitizing dye (SD-9) 1x10-4 mols a mol	l of silver
	Sensitizing dye (SD-10)	
	$3x10^{-4}$ mols a mol	of silver
30	Yellow dye-forming coupler (Y-1)	0.30
	Yellow dye-forming coupler (Y-2)	0.05
<i>35</i>	High boiling-point organic solvent (Oil	-2)
		0.15
	Gelatin	1.1
40	Eleventh Layer: First protective layer (PRO-1)	
	Fine grain silver iodobromide emulsion	
45	(Average grain size: 0.08 μm; AgI conte	nt: 2 mol%)
		0 - 4
50	UV Absorbent (UV-1)	0.10
	UV Absorbent (UV-2)	0 05

39

High boiling-point organic solvent (Oil-1)

0.1

High boiling-point organic solvent (Oil-3)

0.1

Formalin scavenger (HS-1) 0.5

Formalin scavenger (HS-2) 0.2

Gelatin 1.0

Twelfth Layer: Second Protective Layer (PRO-2)

Surface active agent (Su-1)

Alkali-soluble matting agent (Average grain size: 2 µm)

Polymethylmethacrylate (Average grain diameter: 3 µm)

Lubricant (WAX-1)

Gelatin

0.005

0.05

0.04

Respective layers contain, in addition to those components mentioned above, a coating aid Su-2, a dispersion aid Su-3, gelatin hardeners H-1 and H-2, and anti foggants AF-1 and AF-2.

Silver halide emulsions used in this example are as follows.

Em-1: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver iodide content and dispersion of width are 0.46 μ m, 7.0 mol% and 14%, respectively.

Em-2: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver iodide content and dispersion of width are 0.30 μ m, 2.0 mol% and 14%, respectively.

Em-3: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver iodide content and dispersion of width are 0.81 μ m, 7.0 mol% and 14%, respectively.

Em-4: an emulsion containing core/shell-type mono-disperse silver halide grains, of which average grain size, average silver iodide content and dispersion of width are 0.95 μ m, 8.0 mol% and 14%, respectively.

In the above, distribution of width is expressed in the following equation:

Distribution of width (%) = (standard deviation/average grain size) x 100

SD-1

55

5

10

15

20

25

30

35

40

45

SD-2

SD-2

C1

C1

CH=C-CH

CH2) 3SO3

(CH2) 3SO3H

SD-3

SD-3 C_2H_5 $C_$

SD-4

C1 C_2H_5 C_2H_5 C_1 C_1

 $C_{2}H_{5}$ $C_{$

45

SD-6

C2H5

CH=C-CH

(CH₂)₃SO₃ (C₂H₅)₃NH⁺

SD-7

5 CH=C-CH N CH2) 3SO3 (C2H5) 3NH+

15 SD-8

²⁵ SD-9

$$CH$$
 CH
 $CH_2)_3SO_3$
 $CH_2)_3SO_3Na$

35

40

30

20

SD-10

$$CH_3O$$
 CH_3O
 CH_3O
 CH_2
 OCH_3
 CH_2
 OCH_3
 OC

45

C-B (Comparative Coupler) $C_5H_{11}(t)$ 5 $C_5H_{11}(t)$ 10 OCH2CONHCH2CH2OCH3 RC-1 (Comparative Coupler) 15 CONH 20 RC-2 (Comparative Coupler) $QC_5H_{11}(i)$ 25 CONH $OC_5H_{11}(i)$ Cl 30 RC-3 (Comparative Coupler) 35 C₆H₁₃ OCH2CHC8H17 40 45 M-1 $C_5H_{11}(t)$

Cl

M-2

5

15 Y-1

$$\begin{array}{c} \text{CH}_{3}\text{O} & \begin{array}{c} \text{C1} \\ \text{COCHCONH} \end{array} \\ \text{O} & \begin{array}{c} \text{COOC}_{12}\text{H}_{25} \\ \text{N} - \text{CH}_{2} \end{array} \end{array}$$

25

Y-2 30

(CH₃)
$$_3$$
CCOCHCONH—

C₄H₉

COOCHCOOC₁₂H₂₅

40

CM-1 $C_{2}H_{5}O \longrightarrow N=N \longrightarrow NH \longrightarrow CO \longrightarrow C_{18}H_{3}$ $C_{1}O \longrightarrow C_{1}O \longrightarrow C_{18}H_{3}$

 $\begin{array}{c|c} CM-2 & C1 & C1 \\ \hline & N=N & NH & CO & C_{18}H_{35} \\ \hline & C1 & C1 & CO & C_{18}H_{35} \\ \hline & C1 & C1 & CO & C_{18}H_{35} \\ \hline \end{array}$

15

30

50

D-1

OH

CONH

OC14H29

OCH2S

N-N

N-N

CH3

A5

D-2

D-3

D-4

CONH—CONH—COC₁₄H₂₉

CH₂S—CH₃

CH₃

CH₃

OH CONHCH2CH2COOCH3

O CH2S N-N

N-N

C11H23

OH

CONHCH2CH2COOCH3

O N-N

CH2S- N-N

N-N

C11H23

υV-1 5 10 UV-2 15 C_2H_5 20 NH_2CONH — CH— C= O30 H-1 35 40 H-2 $[(\mathsf{CH}_2 \!\!=\! \mathsf{CHSO}_2 \mathsf{CH}_2)_3 \mathsf{CCH}_2 \mathsf{SO}_2 (\mathsf{CH}_2)_2]_2 \mathsf{N} (\mathsf{CH}_2)_2 \mathsf{SO}_3 \mathsf{K}$ 45 $NaO_3S-CHCOOCH_2(CF_2CF_2)_3H$ Su-1 CH₂COOCH₂ (CF₂CF₂) ₃H 50 NaO3S-CHCOOC8H17 Su-2 CH2COOC8H17

Su-3
$$SC-1$$
 OH $C_{18}H_{37}$ (sec) CH_3 OH

Oil-1 Oil-2
$$COOC_{18}H_{37} COOC_{18}H_{37}$$

$$COOC_{18}H_{37}$$

Next, in Sample No.1 above, cyan dye-forming couplers C-A and C-B, which are incorporated in the third and the fourth silver halide emulsion layers, were replaced by equivalent molar amount of Comparative couplers RC-1, RC-2 and RC-3 and the cyan dye-forming couplers according to the present invention as shown in Table-1.

Thus prepared samples were subjected to exposure with white light for 1/100 second through an optical wedge and, thereafter processed according to 'Processing A" and "Processing B"

Processing Steps (at 38°C)

5

10

15

Processing Step Time

Color Development 3'15"

Bleaching 6'30"

Washing 3'15"

Fixing 6'30"

Washing 3'15"

Stabilizing 1'30"

Drying

Ingredients of the processing solutions used in the respective processes are as follows; provided that in "Processing A", "Bleaching Solution A" and in "Processing B", "Bleaching Solution B" were used, respectively.

<Color Developing Solution>

20

35

40

45

50

55

 $4-Amino-3-methyl-N-ethyl-N-(\beta-hydroxyethyl)$

aniline sulfate 4.75 g

Sodium sulfite unhydride 4.25 g

Hydroxylamine 1/2 sulfate 2.0 g

potassium carbonate unhydride 37.5

Sodium bromide 1.3 g

Potassium hydroxide 1.0 g

2.5 g

Add water to make the total volume 1 liter and adjusted pH at 10.2 with ammonia water.

Tri-sodium nitrilo-triacetate monohydrate

<Bleaching Solution A>

Ammonium ferric(III) ethylenediaminetetracetic acid	100 g
Diammonium ethylenediaminetetracetic acid	10.0 g
Ammonium bromide	150.0 g
Acetic acid	10 ml

Add water to make the total volume 1 liter and adjusted pH of the solution at 6.0 with ammonia water.

<Bleaching Solution B>

This solution has the same composition as "Bleach Solution A" except that 2.5 g of sodium hydrosulfite was added to a liter of the above-mentioned "Bleaching Solution A".

<Fixing Solution>

5

10

Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g

Add water to make the total volume one liter and adjusted pH of the solution at 6.0 with acetic acid

<Stabilizing Solution>

15

20

25

30

Formalin(37% aqueous solution)	1.5 ml
Konidax(a product of Konica Corporation)	7.5 ml

Add water to make the total volume one liter.

With respect to the thus obtained dye images produced in Samples 1 through 30 according to the above-mentioned color developing steps, sensitivities of the red-sensitive layer of the Samples were measured using an optical densitometer type PDA-65, a product of Konica Corporation. The sensitivity was obtained in terms of a reciprocal of exposure necessary to give the minimum density plus 0.1 and expressed as relative values as shown in Table 1, in which sensitivity of Sample 1 was normalized as 100.

The term "maximum absorption" means the maximum absorption wavelength(nm) of a sample at a portion of which density measured with red light is 1.0, when it is processed with "processing A".

The term "density difference" in Tables 1 and 2 represents numeral values of the 100-times-multiplied ratio of the maximum densities of the respective samples measured with red light between when it is processed with "processing A" and "Processing B".

The term "storage preservation property before exposure" represents density differences in the fog in the red-sensitive layer of the samples, one of which is placed under atomospheric conditions at 55°C and 65% R.H. for three days and, thereafter subjected to exposure and developing process with "Processing A" and another which does not undergo such experiment.

Results are shown in Table 1 and Table 2.

35

00

40

45

50

Table 1

5	Sample No.	C-A Substi- tution	C-B Substi- tution	Relative Sensi- tivity	Maximum Absorp- tion	Density Differ- ence	Storage Preservation property before Exposure	Remarks
	1	C-A	C-B	100	697	63	0.13	Comp.
10	2	RC-1	RC-2	89	637	93	0.11	Comp.
	3	RC-3	RC-3	85	701	95	0.09	Comp.
	4	RC-3	RC-2	91	702	94	0.10	Comp.
	5	RC-3	I-1	110	700	96	0.09	Inv.
15	6	RC-3	I-2	107	700	96	0.08	Inv.
	7	I-3	RC-2	106	699	96	0.08	Inv.
	8	I-1	I-1	125	698	98	0.07	Inv.
	وا	I-2	I-1	123	697	99	0.07	Inv.
20	10	1-2	I-2	116	698	99	0.05	Inv.
	11	I-2	I-4	115	698	98	0.06	Inv.
	12	I-2	I-6	124	697	98	0.07	Inv.
	13	I-3	I-1	120	697	99	0.07	Inv.
25	14	I-3	I-2	115	698	98	0.06	Inv.
	15	I-3	I-5	119	698	98	0.06	Inv.
	16	I-3	I-14	122	697	98	0.06	Inv.
	17	I-4	I-1	124	697	98	0.07	Inv.
30	18	I-4	I-6	123	697	99	0.07	Inv.
	19	I-4	I-7	120	698	98	0.07	Inv.
	20	I-4	I-12	122	698	98	0.07	Inv.
	21	I-19	I-8	117	698	98	0.07	Inv.
35	22	I-22	I-1	114	698	97	0.07	Inv.
	23	I-33	I-2	112	698	96	0.08	Inv.
	24	I-37	I-1	113	699	96	0.08	Inv.

Table 2

5	Sample No.	C-A Substi- tution	C-B Substi- tution	Relative Sensi- tivity	Maximum Absorp- tion	Density Differ- ence	Storage Preservation property before Exposure	Remarks
₁₀	1	C-A	C-B	100	697	63	0.13	Comp.
.	2	RC-1	RC-2	89	637	93	0.11	Comp.
	3	RC-3	RC-3	85	701	95	0.09	Compo.
-	4	RC-3	RC-2	91	702	94	0.10	Comp.
15	25	RC-3	II-1	110	699	95	0.09	Inv.
	26	RC-3	II-2	106	700	95	0.09	Inv.
	27	II-10	RC-2	107	699	95	0.08	Inv.
	28	II-1	II-1	126	697	97	0.07	Inv.
20	29	II-2	II-1	125	696	98	0.06	Inv.
	30	II-2	II-2	115	697	97	0.06	Inv.
	31	II-2	II-4	120	697	97	0.07	Inv.
ļ	32	II-2	II-6	125	697	98	0.07	Inv.
25	33	II-3	II-1	120	697	97	0.07	Inv.
	34	II-3	II-5	126	696	97	0.07	Inv.
	35	II-3	II-11	124	697	97	0.06	Inv.
	36	II-3	II-19	122	696	97	0.07	Inv.
30	37	II-10	II-1	120	697	97	0.07	Inv.
	38	II-10	II-2	116	698	98	0.07	Inv.
	39	II-14	II-6	119	697	97	0.07	Inv.
	40	II-14	II-10	115	697	97	0.07	Inv.
35	41	II-15	II-1	118	698	97	0.07	Inv.
	42	II-15	II-12	117	698	96	0.07	Inv.
	43	II-24	II-1	111	699	96	0.08	Inv.
	44	II-25	II-1	113	699	96	0.07	Inv.

As obvious from Tables 1 and 2, it is understood that the samples containing the cyan dye-forming coupler according to the present invention have enhanced sensitivity, favorable maximum absorption wavelength, reduced density difference even when it is processed with a fatigue bleaching solution and improved storage preservation property before exposure.

Example 2

40

45

50

55

Sample 2-1 was prepared in the same manner as in Sample 1 of Example 1, except for the following items 1 through 3.

Item 1: 1.0 (g) of Cyan dye forming coupler (C-A) employed in 3rd layer of Sample 1 is replaced with 0.7 (g) of Cyan dye forming coupler (C-B).

Item 2: 0.25 (g) of Cyan dye forming coupler (C-A) and 0.05 (g) of Cyan dye forming coupler (C-B) employed in Sample 1 were replaced with 0.20 of Cyan dye forming coupler (C-B).

Item 3: DIR compound (D-2) employed in 9th layer of Sample 1 was replaced with DIR compound (D-2A).

Samples 2-2 through 2-5 were prepared in the same manner as in Sample 2-1, except that the coupler C-B employed in 3rd and 4th layers of Sample 1 was replaced with the same mols of the coupler shown in Table 3, respectively. The above-mentioned Samples 2-1 through 2-5 were evaluated by the same method disclosed on pages 51 and 52.

5

10

15

20

25

Table 3

Sam- ple	Cyan Dye-Forming Coupler		High Boiling-		Den- sity	_ •	Storage Preser-	Re- marks
No.	No.	Molar	Point Solvent	Sensi- tivity	Change (%)	Dred = 2.0	vation Property,	
		Ratio		(%)		2.0	ΔFog	
2-1	C-B	1	oil-1	100	53	697	0.11	Comp.
2-2	I-1/6-22	0.5/0.5	oil-1	184	97	696	0.07	Inv.
2-3	II-34/6-40	0.5/0.5	oil-1	183	97	696	0.06	Inv.
2-4	I-1	1	A-1	184	96	697	0.06	Inv.
2-5	II-34	1	A-7	183	96	697	0.06	Inv.

As obvious from the results shown in Table 3, it is understood that Samples No.2-2 through 2-5, which are according to the present invention, have enhanced sensitivity, excellent processing stability without shift of the absorption wavelength in the high density portion of the image and improved storage preservation property before exposure.

On the other hand, Comparative Sample 2-1, in which Comparative dye-forming coupler C-B and high boiling-point solvent Oil-1 are used, have good optical absorption, however, density change in the processing with the fatigue bleaching solution and fogging in the storage before exposure are large.

Claims

30

1. A silver halide color photographic light-sensitive material comprising a support and provided thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, wherein said red-sensitive silver halide emulsion layer comprises a compound represented by Formula 1 or Formula 2:

35

40

Formula 1

OR₁
OR₂

$$(R_3)_n$$
OR₂

45

wherein R_1 and R_2 independently represent an aliphatic group, provided that the total number of carbon atoms contained in R₁ and R₂ is 8 or more; R₃ represents a substituent; n is 0 or 1 and R represents an aliphatic group, an aryl group or a heterocyclic group;

Formula 2

50

OH CONH
$$Q_2$$
 Q_3 Q_2

wherein Q_1 and Q_2 independently represent an aliphatic group, provided that the total number of carbon atoms contained in Q_1 and Q_2 is 8 or more; Q_3 represents a substituent; m represents 0 or 1; Q represents an aliphatic group, an aryl group or a heterocyclic group.

The silver halide color photographic light-sensitive material of claim 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula 6:

Formula 6

16 OH NHCONHR₁₁ $R_{12}CONH \xrightarrow{X_{11}}$

wherein R_{11} represents an aryl group or a heterocyclic group; R_{12} represents an alkyl group or an aryl group, provided that R_{12} may form a group capable of forming a dimer or an oligomer with R_{11} or R_{12} ; X_{11} represents a hydrogen atom or a group capable of splitting off upon reaction with an oxidation product of a color developing agent.

3. The silver halide color photographic light-sensitive material of claim 1, wherein said red-sensitive silver halide emulsion layer further comprises a compound represented by Formula A-1:

Formula A-1

 $R_{21}CON < R_{23}$

wherein R_{21} , R_{22} and R_{23} independently represent a hydrogen atom, an alkyl group, a cycloalkyl group or an aryl group.

4. The silver halide color photographic light-sensitive material of claim 1, wherein said -O-Q of said Formula 2 represents an aliphaticoxy group, a heterocyclicoxy group or a

$$-O = (NHCO)_n - R_B$$

$$(R_A)_m$$

wherein R_A represents an alkyl group, a nitro group, an amino group, an alkoxyl group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, m is an integer of 0 to 1; R_B represents a hydrogen atom, an alkyl group, an alkoxyl group, an alkoxycarbonyl group, an alkylamino group, an arylamino group, a nitro group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an aryloxycarbonyl group, n is an integer of 0 to 1.

50 5. The silver halide color photographic light-sensitive material of claim 1, wherein the compound represented by said Formula 1 is represented by Formula 3:

55

20

25

30

35

40

Formula 3

15

20

25

35

40

45

55

5 OCH₂CH< R_4 OCH₂CH< R_5 OCH₂CH< R_5

wherein R_4 , R_5 , R_6 and R_7 independently represent a straight-chained or branched alkyl group, provided that the total number of carbon atoms contained in R_4 through R_7 is 6 through 28; R' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

6. The silver halide color photographic light-sensitive material of claim 1, wherein the compound represented by Formula 2 is represented by Formula 4:

Formula 4

OH CONH—Q5

wherein Q₄ represents a straight-chain, branched or cyclic alkyl group; Q₅ represents a tertiary alkyl group having 4 to 20 carbon atoms or a five member or six-member cyclic alkyl group; Q' represents a substituted alkyl group having 2 to 30 carbon atoms or a substituted phenyl group having 6 to 30 carbon atoms.

The silver halide color photographic light-sensitive material of claim 6, wherein said -O-Q' of said Formula 4 represents an aliphaticoxy group, a heterocyclicoxy group or a

$$-0 \qquad \qquad (NHCO)_{n} - R_{B}$$

$$(R_{A})_{m}$$

wherein R_A represents an alkyl group, a nitro group, an amino group, an alkoxyl group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an alkoxycarbonyl group, an aryloxycarbonyl group, m is an integer of 0 to 1; R_B represents an alkyl group, an alkoxyl group, an alkoxycarbonyl group, an alkylamino group, an arylamino group, a nitro group, a hydroxyalkyl group, a carbamoyl group, a carboxyl group, an alkylsulfonyl group, an arylsulfonyl group, a formyl group, an acylamino group, an aryloxycarbonyl group, n is an integer of 0 to 1.

- 50 8. The silver halide color photographic light-sensitive material of claim 2, wherein the compound represented by Formula 1 or Formula 2 and the compound represented by Formula 6 are contained in a molar ratio of 1:1 to 1:10.
 - 9. The silver halide color photographic light-sensitive material of claim 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of 1 × 10⁻³ mol to 8 × 10⁻¹mol per mol of silver halide.
 - 10. The silver halide color photographic light-sensitive material of claim 1, wherein said compound represented by Formula 1 or Formula 2 is contained in an amount of 1×10^{-2} mol to 8×10^{-1} mol per mol of silver halide.



EUROPEAN SEARCH REPORT

Application Number

U	OCUMENTS CONSID			CLASSIFICATION OF THE		
ategory	Citation of document with indic of relevant passa	ntion, where appropriate, per	Relevant to claim	APPLICATION (Int. Ct. 6)		
A	<u>US - A - 5 302</u> (IRIE et al.) * Totality *	500	1-10	G 03 C 7/305 G 03 C 7/32		
A	JP - A - 04 125 (FUJI PHOTO FIL * Totality *	M CO. LTD.)	1-10			
				·		
				TECHNICAL FIELDS SEARCHED (Int. CL.6)		
				G 03 C		
	The present search report has b	een drawn up for all claims				
	Place of search VIENNA	Date of completion of the s	earch	BECK		
X Y:p	CATEGORY OF CITED DOCUME articularly relevant if taken alone articularly relevant if combined with an ocument of the same category	E : earlier after th other D : docume L : docume	or principle underlyin patent document, but he filing date ent cited in the applic tat cited for other rea	cation isons		
0 1:0 0:1	echnological background 10n-written disclosure ntermediate document	& : membe docum	at of the 22me bateur	family, corresponding		